



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Hideki YAMADA et al.

Serial No.: 09/580,294

Group Art Unit: 1723

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Examiner: KIM, John

For: COMPOSITE SEMIPERMEABLE MEMBRANE

DECLARATION

Honorable Commissioner of Patents and Trademarks

Washington, D.C. 20231

Sir :

I, Hideki YAMADA, declare as follows:

1. I, Hideki YAMADA, have following address:

c/o TOYO BOSEKI KABUSHIKI KAISHA 2-8, Dojimahama 2-chome,
Kita-ku, Osaka-shi, Osaka, Japan.

2. I received Bachelor degree in Department of Applied
Chemistry from Osaka Prefecture University in March, 1985.

3. I have been employed by TOYO BOSEKI KABUSHIKI KAISHA
since 1985, I have been engaged in research of reverse
osmosis membrane and nano-filtration membrane. I am one of
the inventors of the above-identified application, and I am
fully familiar with the subject matter thereof.

4. Based on the experience with the subject matter of above-identified application, the following experiments were conducted to demonstrate that the effects of the present invention cannot be achieved by reverse osmosis membranes disclosed in US 4,259,183 of Cadotte nor US 5,783,079 of Kumano et al.

Together with the Declaration, amendments of claims will be submitted in the United States Patent Trademark Office. It is these amended claims to which I refer in the following description.

The composite semipermeable membrane according to the present invention is prepared controlling the composition of the aqueous amine solution so that the resulting membrane has excellent water permeability, high separation performance, and particularly excellent organic substance removal performance. The preferable range of the concentration of the amine solution is investigated and disclosed in the paragraph on page 17 to 18 of the present specification. Also this is demonstrated in the Example 1, as described in lines 12-14 of page 26 of the specification.

Cadotte as well as Kumano et al. do not disclose at all that the composition of the aqueous amine solution is kept

constant during the preparation of the composite hollow fiber membrane.

Moreover, the composite semipermeable membrane according to the present invention has the sucrose removal of 92% or more due to the above-described preparation method. On the other hand, the references teach or disclose nothing as to sucrose removal.

Experiments

[Experimental methods]

Composite semipermeable membranes were prepared under the conditions described each in the following Experiments A, B, C and D. The composite semipermeable membrane prepared under each condition was sampled 30 minutes or 3 hours after its production was started.

The membrane performance and the infrared absorption intensity ratio T of sampled membranes were evaluated and compared with each sample. Sucrose removal was determined on the same conditions as described on page 22-23 of the present Specification. Calcium chloride removal was determined on the same conditions as described in col. 18 of the Specification of Kumano et al. The infrared

absorption intensity ratio T was determined at 12 points on the membrane outer surface according to the method described on page 23-25 of the present Specification.

[Experiment A]

Supplemental experiment was conducted according to the Example 2 of Kumano et al. Membranes were prepared in the same manner as shown in Figure 2 of Kumano, except that the solution bath 5 was replaced by the solution bath shown in Figure 3.

[Experiment B]

Supplemental experiment was conducted according to the Example 3 of Kumano et al. Membranes were prepared in the same manner as shown in Figure 4 of Kumano.

[Experiment C]

[Experiment D]

Supplemental experiments were conducted according each to Example 1 or 2 of the present application. Membranes were prepared in the same manner as shown in Figure 2 of Kumano, except that the solution bath 5 was replaced by the solution bath shown in Figure 3 and 1 wt% acetic acid was used replacing the aqueous solution of an acid acceptor 20 of Figure 3.

Moreover, 2 different kinds of aqueous amine solutions were added during the preparation of the membranes so that the concentration and the composition ratio of amine solution in the system were kept constant. The compositions and the flow rates of the aqueous amine solutions are shown below.

Aqueous amine solution I

• Flow rate: 0.7 ml/min

• Composition:

Piperazine	2.00 wt%
Triethylene diamine	1.00
Sodium laurylbenzenesulfonate	0.84
<u>Ion exchanged water</u>	<u>96.16</u>
	100 w/w%

Aqueous amine solution II

• Flow rate: 1.0 ml/min

• Composition:

Piperazine	5.56 wt%
Triethylene diamine	2.56
Sodium laurylbenzenesulfonate	0.07
<u>Ion exchanged water</u>	<u>91.81</u>
	100 w/w%

The flow rate of the amine solution was controlled so that the amount of the additional amine solution was in slightly excess of the amount of the solution taken away from the bath by the hollow fiber membrane. The excessive amine solution was overflowed from the solution bath.

If the formation of membrane is conducted over 10 hours or more, the amount of each ingredient contained in the amine solution will be changed depending upon the difference between respective sorbabilities of ingredients to the hollow fiber membrane. Accordingly, the composition in the aqueous amine solution bath should be adjusted. The amine solution in the bath was monitored using gas chromatography and high performance liquid chromatography, and then the flow rate of the additional amine solution was controlled to be appropriate based on the monitored results.

[Results]

The results are shown in TABLE 1 and 2.

The comparative evaluation of membrane performance was made in TABLE 1. TABLE 2 shows the comparative evaluation of the infrared absorption intensity ratio T and the standard deviation (SD) thereof.

[Consideration]

TABLE 1 demonstrates that the composite semipermeable membranes prepared according to the present invention, keeping the composition of the aqueous amine solution constant, have significantly high membrane performance.

Especially the resulting membrane of the present invention maintains its superior performance characteristics not only during the first 30 minutes but also 3 hours after the preparation.

On the other hand, the membranes prepared according to Example 2 and 3 of Kumano do not satisfy the limitation of sucrose removal (92%) recited in the amended claim 1 of the invention. Moreover, the results indicate that the performance of the membrane according to Kumano unstably changes with the passing of time.

It is clear from TABLE 2 that the present membrane has stable infrared absorption intensity ratio T even 3 hours after its preparation, while that of the membrane according to Kumano varies widely 30 minutes as well as 3 hours after its preparation was started.

Considering the changes in properties with time of Kumano membranes on TABLE 1 and 2 together, deteriorated removal performance, increased water permeability and increased standard deviations indicate that the defect of Kumano membrane worsens with the passing of time.

The results of TABLE 2 support the results of TABLE 1 and clearly demonstrate that the composite semipermeable membrane of the present invention achieves highly improved

and stable membrane performance, while the quality of the membranes according to Kumano is uneven.

I, the undersigned, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: Sep. 27, 2001

Hideki Yamada
Hideki YAMADA

TABLE 1



Evaluation Method	Reference 3		Present invention	
Solute	CaCl ₂		Sucrose	
Membrane Performance	Rj (%)	Water Permeability (m ³ /m ² /day)	Rj (%)	Water Permeability (m ³ /m ² /day)
Operating Pressure	@0.5MPa	@0.5MPa	@0.3MPa	@0.3MPa
<i>Ref. 3 (ex. 2)</i>				
30 min after preparation	86.9	0.572	90.8	0.320
3 hours	81.0	0.827	86.5	0.472
<i>Ref. 3 (ex. 3)</i>				
30 min after preparation	92.3	0.551	91.2	0.306
3 hours	86.6	0.903	84.4	0.508
<i>Present invention (ex. 1)</i>				
30 min after preparation	92.3	0.494	95.8	0.266
3 hours	92.0	0.463	95.5	0.272
<i>Present invention (ex. 3)</i>				
30 min after preparation	91.7	0.718	95.3	0.393
3 hours	91.8	0.702	95.4	0.385
<i>Amended claim 1</i>				
			92 or more	0.2 or more

TABLE 2

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O I P E
I A P S
TRADE MARK

Infrared absorption intensity ratio			
	Average	SD	
	T		
Ref. 3 (ex. 2)			
30 min after preparation	0.29	0.082	28
3 hours	0.25	0.116	48
Ref. 3 (ex. 3)			
30 min after preparation	0.34	0.109	32
3 hours	0.27	0.119	44
Present invention (ex. 1)			
30 min after preparation	0.54	0.081	15
3 hours	0.53	0.065	12
Present invention (ex. 3)			
30 min after preparation	0.17	0.017	10
3 hours	0.17	0.022	13
Amended claim 1			
	0.1		